THE REACTION OF DIPHENYLKETENE AND AZIBENZIL WITH OLEFINS

BY

MELVIN IRA KOHAN

A.B., Harvard University, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN THE GRADUATE COLLEGE OF THE
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Introduction

The addition of diphenylketene to styrene, cyclopentadiene, cyclohexene and a few other simple olefins to form cyclobutanone derivatives has been known for several years (1). Prior to this work only a brief and inconclusive attempt had been made to determine whether the formation of a strained four-membered ring imposes a steric requirement on the olefin. With the ultimate hope of developing a reagent capable of characterizing the geometric configuration of unsaturated polymers, this investigation was begun. The first objective was to examine the behavior of a wide variety of olefins towards diphenylketene and define the limits of the reaction. It soon became apparent that the usefulness of the method was seriously limited by the difficulties involved in the preparation and storage of diphenylketene. The possibility of using a precursor of the reagent and generating it *in situ* led to the attempt to treat a reactive olefin, styrene, directly with phenylbenzoyldiazomethane (azibenzil). This procedure was partially successful, and in exploring techniques to improve the method a totally unexpected product, benzhydryl styryl ketone, was observed. Thus a principal effort of this investigation became the examination of this new reaction between azibenzil and olefins.

Discussion

It has been demonstrated that the addition of diphenylketene to olefins is strongly influenced by the nature of the substitution around the olefin. The presence of bulky or negative groups inhibits the reaction. Thus neither maleic nor fumaric ester adds the reagent, and acrylic ester gives an addition product only in very low yield. Earlier work, some of which was repeated in the course of this investigation, has

indicated that tetrasubstituted ethylene derivatives fail to add diphenylketene. Also, the reaction with 1,1-diphenylethylene requires a higher temperature and longer heating period than is necessary with styrene (2).

Diphenylketene shows little tendency to polymerize but is extremely sensitive to atmospheric oxygen as well as traces of moisture in reagents or in the atmosphere. Thus the difficulties inherent both in the preparation and storage of diphenylketene materially limit the possibility of its use as an analytical tool. Since diphenylketene is known to add to quinoline to form an addition compound which can be readily decomposed into the original components (3), it was sought to prepare this reagent by dehydrochlorination of diphenylacetyl chloride with an excess of quinoline. The addition product could not be isolated in good yield; therefore, an attempt was made to treat the dehydrochlorination product directly with an olefin, styrene. The product thus obtained had an elementary analysis which corresponded to the addition of two moles of quinoline to one each of diphenylketene and styrene; infrared analysis indicated a mono N-substituted amide structure. Dehydrochlorination was next effected with an equimolecular amount of triethylamine, and the direct treatment of this reaction product with styrene gave a fifty-three per cent yield of the expected 2,2,3-triphenylcyclobutanone.

The reaction of both azibenzil and diphenylketene with certain pyrrole derivatives has been shown to yield the same products (4). The reaction of azibenzil with styrene was therefore examined, and it was found that when ether or acetone solutions of the reagents were heated under reflux, the expected cyclobutanone derivative is obtained but in less than thirty-five per cent yield. When a dioxane solution was heated for two to five hours the cyclic ketone was produced in a maximum yield of fifty-eight per cent, but heating for forty-eight hours gave a product made up about equally of 2,2,3-triphenylcyclobutanone and benzhydryl styryl ketone $[(C_6H_5)_2CHCOCH = CHC_6H_5]$. After ninety-six hours only the linear α,β-unsaturated ketone was formed. The structure

of the linear ketone was established by comparing its properties with an authentic sample prepared by condensation of benzaldehyde with 1,1-diphenylacetone. Compounds known to facilitate the decomposition of aliphatic diazo compounds such as iodine, copper and acids were added to the reaction mixture and were found to promote the formation of the cyclobutanone derivative. The addition of a weak base such as triethylamine, depending on the amount added, gave no product or low yields of the cyclic compound. The use of potassium *t*-butoxide resulted in a mixture which did not appear to contain either the cyclic or linear ketone. Higher boiling solvents varying in polarity were then employed in the attempt to reduce the reaction time. In dibutyl ether or *o*-xylene less time was required to obtain the linear ketone as the sole product, but the yields were lower; no product could be isolated when the reaction was carried out in dimethylformamide.

The observed effect of time on the composition of the azibenzil-styrene reaction product suggested that the cyclobutanone compound was formed initially and then slowly converted to the linear unsaturated ketone, but the heating in dioxane and in dibutyl ether of a sample of pure 2,2,3-triphenylcyclobutanone failed to yield any benzhydryl styryl ketone.

Azibenzil was treated with a variety of other olefins and styrene analogs, and no reaction was observed in the following cases: dodecene-1, methyl erucate, ethyl acrylate, β-bromostyrene, methyl cinnamate, cyclohexene, 2-vinylpyridine, 1,1-diphenylethylene, phenanthrene, 1,2-dihydronaphthalene, *o*-chlorostyrene, *m*-nitrostyrene, *p*-nitrostyrene and 1-vinylnaphthalene. With ethyl crotonate, propenylbenzene and α,*p*-dimethylstyrene the reaction products involved mixtures which were shown in each case to contain compounds for which spectroscopic and analytical examination indicated a diphenylketene-olefin adduct structure but not that of a cyclobutanone or α,β-unsaturated ketone. Cyclopentadiene yielded only the corresponding cyclobutanone derivative. *p*-Vinylbiphenyl, *p*-methoxystyrene and *p*-ethoxystyrene gave in seventeen to

twenty-nine per cent yield benzhydryl *p*-phenylstyryl ketone, benzhydryl *p*-methoxystyryl ketone and benzhydryl *p*-ethoxystyryl ketone respectively. In the last two instances it was not possible to obtain a cyclobutanone derivative even when the reaction mixture was heated for short periods or in the presence of iodine or sulfuric acid.

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VITA

The author was born in Boston, Massachusetts, on March 11, 1921. His elementary and high school education was received in the public schools of Cambridge, Massachusetts. Following graduation from Harvard University in June, 1942, he was employed by the Electrochemicals Department, E. I. du Pont Company, Niagara Falls, New York, until entering the Army of the United States in August, 1944. He was married on February 6, 1943, and has one child, a son born on October 5, 1944. After returning to his former position for one year, he entered the University of Illinois in the fall of 1947 where he has held special research assistantships.

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